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APPLICATION NUMBER: ***60/444,183***
FILING DATE: ***February 03, 2003***

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02/03/03 jc806 U.S. PTO

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No.

J1000 U.S. PTO 60/444183

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
Murray	FIGOV	Ra'anana, ISRAEL

☐ *Additional Inventors are being named on the ______ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

CTP-INKJET USING SWITCHABLE POLYMER

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☑ Specification *Number of Pages* 15

☐ Drawing(s) *Number of Sheets*

☐ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number

☐ Other (specify)

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☐ A check or money order is enclosed to cover the filing fees

☐ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number:

☐ Payment by credit card. Form PTO-2038 is attached.

FILING FEE AMOUNT ($): $210.00

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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☑ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: ______

Respectfully submitted,

SIGNATURE [signature]

Date 02/03/2003

TYPED or PRINTED NAME Edward LANGER

REGISTRATION NO. *(if appropriate)* 30,564

TELEPHONE 972-3-710-3311

Docket Number: 1673

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

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11000 U.S. PTO
60/444183
02/03/03

Date: February 3, 2003

The Commissioner of Patents and Trademarks
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Dear Sir,

Enclosed herewith for filing is the following **PROVISIONAL** patent application:

Title of Application: **CTP-INKJET USING SWITCHABLE POLYMER**

Inventor(s): Murray FIGOV, Ra'anana, Israel

Specification: 15 pages

Docket No.: 1673

TOTAL FILING FEE: $210.00 ($160.00 Provisional filing fee and $50.00 Late Filing Fee)
X Payment will follow

Also enclosed herewith for filing are:

X Provisional Patent Application Cover Sheet (PTO/SB/16)

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CTP-INKJET USING SWITCHABLE POLYMER

BACKGROUND OF THE INVENTION

Offset lithographic printing has remained a most popular method of printing for many years. An important reason for this is the relative ease with which offset lithographic printing plates can be produced. Currently, the most widely used method for plate preparation is that which utilizes specially prepared masking films through which pre-sensitized printing blanks are selectively hardened or softened (according to the chemistry of the plate) by exposure to ultra violet light. The plate then undergoes a development process, during which the more soluble regions of the coating on the plate are washed away. A detailed description of the system and the plates used can be found in Chapter 20 of the book " Printing Materials: Science and Technology" by Bob Thomson 1998, published by Pira.

In recent years, various considerations have arisen that point to advantages for modification of hitherto generally accepted practices. With the advent of computers, information for printing is prepared digitally and it has become preferable to use this digital information as directly as possible in plate preparation. One obvious way would be to eliminate the masking film. Not only are these films a source of expense, but the most widely used films are based on silver chemistry whereby the exposure and handling of the film must be in a light-excluding environment. In addition, the exposed film must be processed with chemical solutions which are unstable, messy and environmentally

problematic. One answer is to be found in computer-to-plate systems whereby the offset litho plates are directly imaged with a source of electromagnetic radiation which is modulated to correspond to the digital information from the computer. Thus the film intermediate is completely eliminated. In general, such plates still need processing by solution, although attempts are being made to develop computer-to-plate systems that are processless. The subject of computer-to-plate can be found in the above quoted book in Chapter 21.

US Patent No. 5,339,737 to Lewis et al describes the processless preparation of offset litho printing plates, wherein the upper layer or layers of the plate are ablated away. The upper layer is either oleophobic, for waterless plates, or hydrophilic, for conventional wet process plates. The substrate is oleophilic in both cases. US Patent No. 5,353,705 to Lewis et al is similar to the previous patent but describes additional layers for secondary partial ablation. US Patent No. 5,487,338 to Lewis et al is also similar, but includes reflective layers. All of these inventions involve multiple layered plates which are expensive to produce. Also it is more difficult to maintain a consistent standard of quality from plate to plate. Moreover, they utilize laser imaging systems which are in themselves costly. In US Patent No. 5,713,287 Gelbart introduced the use of a single layer that could be modified by laser imaging to change its nature from being oleophilic to being hydrophilic. Coatings that behave in this way – whether the change is from oleophilic to hydrophilic or from hydrophilic to oleophilic - have become known as layers of switchable polymers. Offset plates using this idea would require no further treatment after imaging and before printing on a press. As a further example of this principle US 2002/0197563 by Zheng et al. describes a thermal switchable composition.

It is obviously desirable to have a plate-making process with the utmost simplicity, the elimination of all chemical processing and a minimal cost for the equipment for plate imaging and for the plate production itself. The process should also be fast.

A technology that has been rapidly maturing in recent years may be seen to offer solutions to easy and inexpensive plate production. This is the technology of inkjet printing.

Inkjet is a non-impact printing process whereby ink is squirted through very fine nozzles and the resultant ink droplets form an image directly on a substrate. There are two main types of ink jet process. In one process, usually termed continuous ink-jet printing, a stream of ink drops are electrically charged and then are deflected by an electric field either directly or indirectly onto the substrate. The viscosity of inks used in such systems are typically 2 or 3 centipoises. In the second process, usually called Drop on Demand (DOD) ink-jet printing, the ink supply is regulated by an actuator such as a piezoelectric actuator. The pressure produced during the actuation forces a droplet through a nozzle onto the substrate. Inks for DOD ink-jet printing do not need to be conductive and their viscosity is typically between 2 and 40 centipoises.

The application of inkjet to produce printing plates is an idea which can be traced back to the origins of the inkjet process. In US Patent No. 2,512,743 assigned to the Radio Corporation of America, Clarence W. Hansell, the inventor of the DOD method described in this patent wrote "The invention may also be used for spraying acids and chemicals for etching of printing plates.....". Although the general concept was disclosed here, no further details were given. US Patent No. 4,003,312 to Gunther details methods

of inkjet offset lithographic platemaking, but the plate substrate is confined to silicone surfaces for driographic (waterless) printing, which had been at that time recently invented (see US Patent No. 3,511,178 - Curtin). UK Patent No. 1431462 describes the use of a continuous jet process to image a coated plate by hardening the coating with a reactive ink. The unhardened background areas are then washed away. JP56105960 to Nakayama et al., assigned to Fuji Photo Film (1981), includes the use of heat activated hardening material in oleophilic ink jet inks, forming the image areas on hydrophilic substrates. The substrate may or may not be coated.

Although the idea of plate-making by inkjet has a long history, commercial success in the field has been limited by the lack of maturity of the inkjet process itself. Development of plate-making followed the developments in inkjet. US Patent No. 4,833,486 to Zerillo (assigned to Dataproducts) utilizes a hydrophobic solid ink-jet ink (containing waxes), which is held at a sufficiently high temperature to jet it through a DOD head (This solid ink technology is more fully described in US Patents No. 4,390,369, 4,484,948, and 4,593,292.) The substrate is a hydrophilic offset plate - either paper or aluminum - onto which the image is jetted. When the ink hits the plate it immediately cools and solidifies. One problem of such an approach is the difficulty of obtaining sufficiently good adhesion of the waxes of the ink to the plate to run multiple impressions during lithographic printing.

EP503621 (Applicant NIPPON PAINT CO) contains two approaches. One approach describes jetting inks onto a pre-sensitized plate, which then needs further treatment, including a developing stage with a liquid developer. The other approach uses a non-presensitized plate and the inkjet ink is photosensitive so that it can be hardened on

the plate.

EP533168 by Nippon describes the use of a photopolymeric-based inkjet ink together with an ink absorbing layer on the litho plate surface.

EP697282 to Leanders (Agfa) describes a two-component system whereby one reactive component is in the ink and the other in the litho plate surface, so that when the ink hits the plate it produces an oleophilic reduced silver image that can be used in the offset printing process.

US Patent No. 5,495,803 by Gerber describes imaging a coated, pre-sensitized plate with a UV opaque hot melt inkjet ink and using the ink as a photo-mask to expose the plate. The unexposed pre-sensitized polymer and the ink are subsequently removed by washing.

US Patent No. 5,738,013 to Kellet describes an ink-jet plate-making process involving the use of a reactive inkjet ink which is bonded to the litho plate by a chemical reaction activated by radiant energy. This assumes that such inks have very good stability at room temperature so that no jet blocking will occur, yet have good reactivity at high temperatures so that the ink becomes insoluble with good adhesion to the offset plate and with good oleophilic properties.

Because the basic principles of inkjet imaging of printing plates have been so well covered by prior art, most recent patents have been confined to very specific ways of achieving such plates. Thus Kato et al. utilizes oil-based inks of a variety of types in plate formation (US Patents No. 6,106,984, 6,174,936B1, 6,184,267B and 6,197,847B1).

US Patent No. 5,820,932 to Hallman et al (Sun Chemicals) describes a variety of reactive inks and processes, using two inkjet heads to form the print image on a plate

substrate.

Newington et als. (WO 00/37254) and Nitzan et als (WO 01/49506) both use aqueous emulsions as the ink jet fluids. These emulsions have oleophilic particles dispersed in aqueous media and are suitable for ink jetting. On deposition onto the hydrophilic substrate, which is anodized aluminum, the emulsion particles coalesce, forming an insoluble oleophilic image. Such an image can be hardened by heating to increase the adhesion of the image to the plate surface, thus giving a larger number of acceptable printing impressions. Nitzan claims better control of dot size by providing a thin cationic surfactant coating on the surface of the anodized aluminum.

US Patent No. 6,471,349 (Aurenty et al.) describes jetting a non-aqueous ink onto an anodized aluminum substrate, which may or may not be further treated. The ink adheres both physically and chemically to the surface of the substrate. US 6,472,054 (also by Aurenty et al.) uses aqueous or non aqueous inks containing partially neutralized acidic polymers to form the image, which is described as bonding to the plate substrate in a manner similar to that of the previously mentioned patent.

Methods involving the use of uncoated anodized aluminum suffer from the problem of poor surface stability. The surface of uncoated anodized aluminum is oxidized with time and loses its hydrophilic properties. This is well known in the art and is remedied by preserving the plate with a layer of gum or gum substitute. Moreover, the highly hydrophilic nature of the surface and the graining which produces an uneven surface in order to give good fount retention increases the spreading of the ink jet ink on the plate surface with a loss of resolution. The cationic layer as described by Nitzan for improving resolution will not prevent the surface oxidation effect and therefore a

customer would have to have plates supplied with a preservative layer, which would then have to be washed off before application of the surfactant. Where the plates described in patents mentioned above use uncoated anodized aluminum on which to jet the ink, the same problem will occur and can be remedied by the cumbersome process of gumming and de-gumming.

Methods of ink jet plate-making such as that described in US Patent No. 6,315,916 B1, whereby a pre-sensitized plate has an ink jet image deposited onto it and whereby this image reacts with the sensitized layer, require a subsequent process of development in a processor. Development is a well-known method used with standard pre-sensitized plates but it is a method which users would like to avoid. It utilizes highly alkaline liquids which may have problems of drainage disposal in many countries. The processing liquids are subject to reaction with the air and must be changed every few weeks; also the processing liquids gradually become contaminated with the material that they are removing. They often form sludges and the processor needs to be thoroughly cleaned out periodically. It is no wonder that the industry is seeking out processless plates. Moreover, pre-sensitized plates used in this inkjet method are light sensitive and have to be handled in subdued or yellow light.

Thus, whilst there have been prior arts attempts to use the inkjet process for imaging printing plates, present solutions are not completely satisfactory.

SUMMARY OF THE INVENTION

The present invention provides an inexpensive and simple method of producing an offset lithographic printing plate by means of the ink jet process, using particular coated substrates which can be switched from being hydrophilic to being oleophilic by a switching material situated in the jetted inkjet fluid, to give sharp ink jet images, long run lengths and long shelf life.

The present invention further provides a printing plate imaged by inkjet that then requires no liquid or extra treatments other than optional warming to increase the number of good impressions.

When the term "imaging" is used in this patent, it refers to the process of selectively depositing ink jet fluid onto an offset printing blank – the selected area corresponding to signals generated from a computer and representing a pattern, with the intention of producing multiple copies from that image.

DESCRIPTION OF THE INVENTION

The essential components of the present invention are a hydrophilic coating combined with aqueous inkjet fluids, in which is incorporated a switching chemical that on contact with the substrate coating during the imaging process, with or without heating, causes the substrate coating to switch from hydrophilic to oleophilic.

When the term "imaging" is used in describing this invention, it refers to the process of selectively depositing ink jet fluid onto an offset printing blank – the selected area corresponding to signals generated from a computer and representing a pattern with the intention of producing a master from which multiple copies can be made by use on a printing press.

The type of substrate coating used is described in co-pending Provisional Application No. 60/432,240 filed Dec. 11, 2002 (commonly owned with the present application and hereby incorporated by reference.)

Preferably, the coating used is made up of commercially available materials and does not contain any specially synthesized components. This minimizes costs and eliminates the need to have new chemicals enduring long and expensive processes that are now in place to ensure that the materials are safe to use from environmental and health considerations. Preferably, all of the ingredients have been tested for environmental and health suitability. The solvent used to apply the coating is water - once

again with environmental and health considerations in mind. The coating used contains a number of essential components. These are as follows; -

Polyvinyl alcohol. This is a material available from a number of suppliers and in a variety of grades defined by such properties as molecular weight. It should be present in between 1% and 15% by weight of the total solid content of the layer and is preferably at 4 to 6%. It is dissolved in water and added to the complete formulations as a solution. The preferred grade has a relatively low molecular weight (22,000), but higher molecular weights can be used.

Polyacrylic acid. It should be present in between 30 and 60% of the total solids by weight- preferably within the range of 40 to55%. This too is a material generally available and is sold in a number of grades distinguished once again by molecular weight. Here again, a low molecular weight (35,000) is preferable and is purchased and used as an aqueous solution.

Oleophilic water-based emulsion. Although the coating is designed to be hydrophilic, it has been found that such emulsions that might be claimed to be oleophilic and water resistant are essential as part of the system, to give a combination of hydrophilic properties good adhesion to substrates combined with resistance to the fount solution. The polyvinyl alcohol and the polyacrylic acid as such are water soluble and without other ingredients any coating containing just these ingredients would be washed away by the fount solution. Such emulsions must be present in amounts from 30% to 55% by weight of the solids. Only emulsions with a pH of 7 or less can be used as those of higher pH do not show good compatibility in the system. The preferred type of emulsions are those based on vinyl acrylics. For instance, Flexobond 325 is a vinyl acetate-acrylate

copolymer with a pH range of 4 to 6. The manufacturers of this emulsion recommend it for water resistance. Wallpol 40-36 is a vinyl acrylic latex polymer with a pH of 5.0, used in paints and is described as high scrub. Both of these emulsions are particularly of use in this system.

Wetting agent. It is well known that such ingredients are essential to the production of good coating properties on substrates. However, it has been found that silicone surfactants such as the polyether modified polydimethyl siloxane BYK346 contribute to the hydrophilic properties of the coating and therefore, such materials should be present in amounts from 0.5% to 5% of the total solids by weight.

Amino resin cross-linkers. Such resins must be water soluble even if they are supplied as alcohol solutions. Whereas the other ingredients must be acidic, it has been found that this is not essential in the case of the amino resins. These are present in amounts below 10% of the solids by weight and preferably between 2 and 7%. An example of a preferred resin is Cymel UFR-60. It is believed that such resins function in the system by cross-linking primarily with the polyvinyl alcohol. The problem which this type of complex formulation solves is to produce a coating which is extremely hydrophilic and yet is fount resistant and has good adhesion to substrates. A large amount of aminoplast gives very good substrate adhesion and fount resistance, but especially where a conventional catalyst for the aminoplast is included (such as toluene sulfonic acid) the layer is not hydrophilic. Thus it has been found that for this application, contrary to regular practice, the quantity of aminoplast is limited and aminoplast catalysts must be omitted. Adhesion to the substrate is also affected by the temperature at which the coating is dried. The higher the temperature, the more likely the coating is to become oleophilic. It has been found by

omitting the catalyst that coatings with the ingredients balanced as specified give films that are especially strongly bonded to anodized aluminum and to completely untreated aluminum and can be heated to temperatures in the range of 160°C to give optimum adhesion combined with excellent hydrophilic properties.

Optional added ingredients are hydrophilic extenders such as clays.

It is a preferred type of formulation where each and every ingredient has been tested and given some kind of approval rating for health and Safety and environmental effects by an authorized authority.

Coatings made from the above-defined ingredients are applied to typical printing plate substrates such as grained anodized aluminum, polyester and untreated aluminum. Untreated aluminum is the preferred substrate as it is less expensive than grained anodized and metal-based plates are preferred to polyester plates by many printers. Coating weight is between 0.3 grams per square meter and 4 grams per square meter and is preferably in the range 0.5 to 2 grams per square meter.

It has been found that a diverse selection of water-soluble materials can be used to switch the coating from being hydrophilic to being oleophilic. Materials were tested by dissolving the chemical under test in water, to give a 6% by weight solution. It was then applied to the coated substrate by writing with a wooden toothpick. The imaged plate was then heated at 160°C for 4 minutes and then rubbed successively with fount and litho ink. Where there was writing, if the chemical caused a switch it took ink. Of the materials tried in this test, sulfonic acids appeared to act as switches, whereas carboxylic acids did not. Iron and copper salts appeared to work. Whilst no overall theory is advanced, it is possible that the switching materials specifically catalyze a condensation reaction

between the aminoplast and the polyacrylic acid and the resulting cross-linked molecules are then oleophilic.

It is possible to incorporate small quantities of these switching materials into ink jet inks for use in both the DOD and continuous types of ink jet printing processes This may be done using commercially available aqueous inkjet inks - either dye based or pigment based, or can be used in specially formulated inks starting from scratch.

It is also possible to combine the microencapsulated ink with an ink-switchable material to ensure a long running plate. If during the course of long runs on the printing press, the microencapsulated ink becomes detached from the plate, the newly exposed surface situated under the image areas of the ink jet ink which would have been switched to be oleophilic would still retain the offset ink so that no detectable image deterioration would occur. Microencapsulated materials can be used as described in our Provisional application Number 60/432,240. As discussed in that application, it is possible to print each plate with a colored ink matching the color of the printing ink to be used with that specific plate, so that for instance the printer who wishes to prepare a set of color separations may do so by preparing each separation from the corresponding colored ink. This way, once the plates have been prepared, they cannot be confused, avoiding the possibility of printing a separation with the wrong colored ink.

Such systems as described above can be adapted for imaging directly on the printing press and for use as the basis of a computer-to-press application. Such an application was described in the IS&T NIP14 1998 International Conference on Digital Printing Technologies by Huber et als (page 646). Huber describes the use of hot melt ink, inkjetted onto anodized aluminum. He attempted to use the master cylinder of a

printing press for printing by means of the phase change ink jet ink on the surface. After the printing run was completed, the image was erased and a new image produced. The application that he worked on was only able to produce 100 impressions.

It is possible, using the present invention, to spray the hydrophilic coating onto an unanodised aluminum on a master cylinder, to ink jet image it, heat the plate to ensure optimum image production and run multiple impressions. The coating on the substrate can be removed with for instance an aqueous solution of an ethanolamine, washed and dried and re-used over and over again.

EXAMPLE

A 12% solution of polyvinyl alcohol (Molecular weight approximately 22,0000) in de-ionized water was prepared by heating with stirring. A 35% solution of Polyacrylic acid (average molecular weight 100,000) was used. The following formulation was made up. Ingredients are quoted in parts by weight and were added in the order shown. After each addition the mixture was high speed stirred to ensure good mixing:

Polyvinyl Alcohol Solution (12%)	12.76 parts
Polyacrylic Acid Solution (35%)	35.82 parts
Water	25.23 parts
Walpol 40-136	23.47 parts
BYK 346	1.49 parts
Cymel UFR-60	1.23 parts

The mixture was coated onto 150 micron thick aluminum foil and dried in the oven at 120°C for 4 minutes, giving a total coating thickness of approximately 1.7 grams per square meter.

An Epson T5432 dye based magenta ink was modified by the addition of 6% by weight of naphthalene 1:5 disulfonic acid and used in an Epson Stylus 7600 ink jet printer. The sheet prepared above was passed through the four-color printer using only the modified magenta ink. The resulting imaged plate was heated to 160°C for 4 minutes and then run on a Heidelberg GTO printing press to give clear good impressions.

Cymel UFR -60 methoxymethyl methylol urea (88% solution in isopropanol)

Walpol 40-136 Vinyl Acrylic latex polymer (55% in water)

Sources of Raw Materials:

BYK 346. BYK-Chemie GmbH, Postfach 100245, Wesel

Cymel UFR-60 Cytec Industries. Five Garret Mountain Plaza, West Patterson, NJ. USA

Walpol 40-136. Reichold, Inc, Research Triangle Park, NC, USA.